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RAPID COMMUNICATION

Supercritical CO₂ impregnation process applied to polymer samples preparation for dynamic nuclear polarization solid-state NMR

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Abstract

In this study, supercritical CO₂ (scCO₂) was used to impregnate polymers with paramagnetic polarizing agents to prepare samples for dynamic nuclear polarization (DNP) solid-state NMR (ssNMR) experiments. As a proof of concept, we impregnated polystyrene samples with bTbK, which stands for bis-TEMPO-bisketal where TEMPO is 2,2,6,6-tetra-methylpiperidin-1-oxyl. Substantial DNP signal enhancements could be measured on DNP-enhanced ¹H → ¹³C cross-polarization (CP) magic-angle spinning (MAS) spectra recorded at 9.4 T and ~100 K, reaching a maximum value of 8 in the most favorable case, which appeared comparable or even higher than what is typically obtained on similar systems for former sample preparation methods. These results highlight the potential of scCO₂ impregnation as an efficient and possibly versatile methodology to prepare polymer samples for DNP ssNMR investigations.

KEYWORDS

dynamic nuclear polarization, solid-state NMR, supercritical CO₂ impregnation

1 | INTRODUCTION

Dynamic nuclear polarization (DNP) has become a technique of choice for improving the sensitivity of solid-state nuclear magnetic resonance (ssNMR) experiments.^[1–11] DNP enhances nuclear magnetization through the microwave (MW)-driven transfer at cryogenic temperatures of electron spin polarization to nuclei via paramagnetic centers, which are typically referred to as polarizing agents (PAs). In principle, whereas PAs can either be contained in (endogenous) or added to (exogenous) the material

under investigation, the best DNP sensitivity enhancements obtained so far have been observed when using exogenous PAs, although there are some notable exceptions,^[12–15] including recent work where endogenous radicals were generated in the sample by γ -ray irradiation.^[16,17] As a matter of fact, the design of efficient PAs has been the subject of extensive research over the last few years, which has led to the synthesis of a wide range of biradicals exhibiting increasingly complex molecular structures (e.g., TOTAPOL,^[18] bTbK,^[19] TEKPol,^[20] AMUPol,^[21] HyTEK2,^[22] cAsymPol-POK,^[23]

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and nitroxyl–trityl biradicals^[24]). For model compounds, ¹H DNP signal enhancements of ~200 at 9.4 T and 100 K can now be easily reached. These enhancements were even shown to peak at ~500 in some specific experimental conditions (i.e., ~75% of the maximum value).^[25] As a result, high-field DNP can potentially increase the sensitivity of ssNMR experiments dramatically, leading to unprecedented applications for the structural analysis of biological solids^[11] or the characterization of materials,^[6] including polymer materials.^[26,27]

Overall, key to the success of any DNP experiment is sample preparation. In fact, exogenous PAs should ideally be homogeneously dispersed in the material under investigation to avoid PAs clustering or aggregation and achieve substantial DNP signal enhancements. Although several techniques have been reported in the literature so far, it is fair to say that no universal method is available yet, even though the incipient wetness impregnation method introduced by Lesage et al.^[28] has already proved versatile for a range of systems. In other words, investigators should try and adapt the various available protocols to their specific case, and this may prove daunting. This is especially true for polymer materials where careful optimization of sample preparation conditions is typically required to achieve meaningful results,^[29–36] with no guarantee of success in the end. In parallel, supercritical CO₂ (scCO₂) impregnation has been used for a long time in the field of polymer materials to impregnate specific components (e.g., additives, active pharmaceutical ingredients, dyes, and organic metallic complexes) in a polymer matrix.^[37] scCO₂ impregnation (hereafter referred to as i-scCO₂ for brevity) is a versatile methodology that consists of impregnating bulk materials (e.g., polymers) with a solute of interest that is first solubilized in a supercritical fluid (CO₂). With respect to liquid-phase impregnation, i-scCO₂ typically allows faster in-depth and more homogeneous impregnation at moderate temperatures (35–60°C) thanks to the unique properties of supercritical fluids (e.g., low viscosity, low surface tension, high density, and increased diffusivity). Furthermore, scCO₂ is sorbed by polymers under pressure, inducing their plasticization and swelling.^[38,39] These phenomena enhance impregnation and ensure in many cases a molecular dispersion of the solute in the polymer. i-scCO₂ has already been applied to impregnate a large range of polymer materials (polyacrylate, polyethylene, polycarbonate, polyamide, polypropylene, polyurethane, etc.),^[38] especially in biomedical applications where complex (co)polymers are regularly impregnated with bioactive molecules, such as antioxidant or antibiotic compounds.^[40,41] It has, however, never been used in the context of DNP ssNMR.

In this work, we show that scCO₂ can be successfully used to impregnate biradicals in polymer samples for

DNP ssNMR studies. For this proof of concept, we selected economically more affordable but less efficient bTbK biradicals (as compared, for instance, to TEKPol biradicals). Still, significant DNP signal enhancements could be measured in ¹H → ¹³C cross-polarization (CP) magic-angle spinning (MAS) spectra, which appeared comparable or even higher than those obtained in the literature on analogous systems, suggesting that i-scCO₂ could reveal to be an efficient preparation method for the DNP ssNMR analysis of polymer samples.

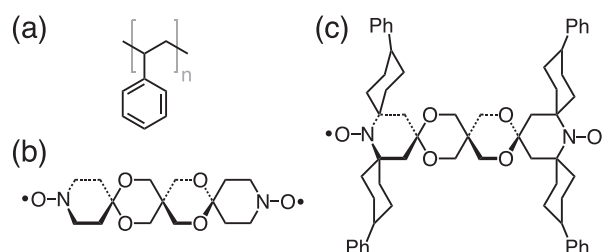
2 | MATERIALS AND METHODS

2.1 | Samples

Both polystyrene (PS) samples (*M_n* 35 and 280 kg mol⁻¹) were obtained by anionic polymerization and were purchased from Sigma-Aldrich, whereas TEKPol was acquired from Cortecnet. bTbK was synthesized as described elsewhere.^[19] The molecular structures of these compounds are shown in Scheme 1. All chemicals were used as such without further purification. Film casting (FC) samples were prepared by solubilizing ~100 mg of polymer into 1 ml of dichloromethane in a Teflon™ beaker; after polymer solubilization, a bTbK solution in dichloromethane was added to the polymer solution, and the solvent was subsequently evaporated at room temperature. The targeted bTbK concentration in the FC samples was 10 μmol g⁻¹, which has been previously shown to yield optimal results in terms of DNP sensitivity enhancement for polymers.^[29]

2.2 | DNP ssNMR experiments

All DNP ssNMR experiments were recorded on a Bruker 9.4-T wide-bore magnet (400 and 100 MHz for the ¹H and ¹³C Larmor frequency, respectively) operated by an AVANCE-III NMR spectrometer. The spectrometer was equipped with a Bruker 3.2-mm low-temperature



SCHEME 1 Molecular structures of the compounds under study: (a) polystyrene, (b) bTbK, and (c) TEKPol

triple-resonance DNP $^1\text{H}/^{13}\text{C}/^{15}\text{N}$ CP MAS probe. The sample temperature was ~ 100 K, and the spinning frequency was set to 10 kHz. The spectrometer was equipped with a gyrotron that allowed MW irradiation of the sample. Specifically, the field sweep coil of the NMR magnet was set so that MW irradiation occurred at the maximum DNP enhancement of TOTAPOL (263.334 GHz).^[18] The estimated power of the MW beam at the output of the probe waveguide was ~ 4 W. During the CP MAS experiment, the MW irradiation field was either turned *off* or continuously *on*. During CP, the amplitude of the ^1H contact pulse was linearly ramped from 50% to 100% of the nominal ^1H radio-frequency (RF) field strength (90 kHz),^[42] whereas the amplitude of the ^{13}C CP spin-lock RF field was 50 kHz. The CP contact time was adjusted to 1 ms, and SPINAL-64 was used for ^1H decoupling (with a ^1H RF field strength of 90 kHz). The 90° ^1H RF pulse length was 2.8 μs . In all experiments, 1024 complex data points were acquired with a 30-kHz spectral window, leading to an acquisition time of 34.4 ms. The number of scans was set to 8. The recycle delay was set to five times the ^1H MW-driven polarization buildup time constant (τ_{DNP}) of the samples measured with a ^1H saturation-recovery pulse sequence (using a train of 50 90° ^1H RF pulses separated by 1 ms) with the MW field *on*. All experiments were conducted using 3.2-mm sapphire MAS rotors sealed with TeflonTM inserts and closed with zirconia caps, yielding an active volume of ~ 20 μl and a typical mass of polymer sample in the rotor between 10 and 20 mg (depending on the polymer sample morphology). Finally, note that DNP signal enhancements (ϵ) were herein exclusively defined as the ratio of the intensities of the ^{13}C resonances in the $^1\text{H} \rightarrow ^{13}\text{C}$ CP MAS spectra recorded with (I_{ON}) and without (I_{OFF}) microwave irradiation ($\epsilon = I_{\text{ON}}/I_{\text{OFF}}$).

This simple definition is typically used to quantify the DNP signal enhancement, even though it may not be the most appropriate to quantify the actual *sensitivity* gain brought about by DNP.^[4]

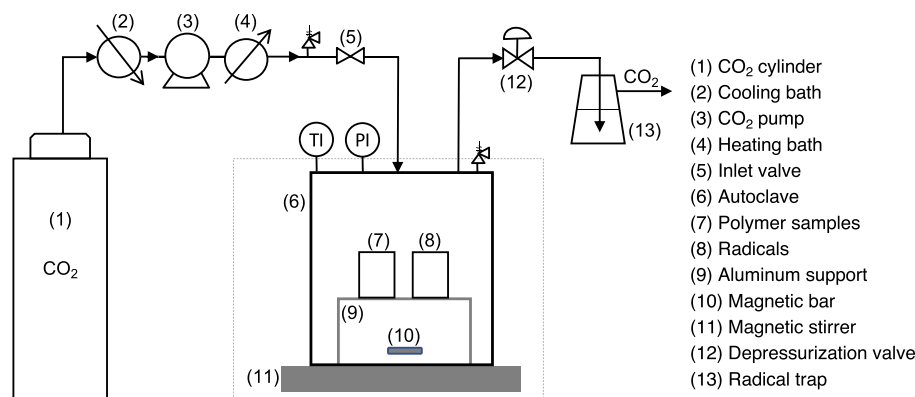
2.3 | Supercritical CO₂ impregnations (i-scCO₂)

All scCO₂ impregnation (i-scCO₂) experiments were performed in a batch mode using the experimental setup described in Scheme 2. It is mainly composed of a 125-ml high-pressure cell (Top Industrie S.A., France) and a high-pressure liquid CO₂ pump (Milton Roy, France). The autoclave is positioned on a magnetic stirrer to ensure faster solubilization and homogenization of the biradicals in scCO₂ and immersed in a thermostat bath to regulate its temperature.^[4] In a typical experiment, known

quantities of polymer samples and of the biradicals were placed on an aluminum support inside the high-pressure cell to separate them from the stirrer bar. Polymers were protected with a paper filter to avoid radical deposition on their surface during the depressurization step. Samples were impregnated either as powders or as films (prepared using the same FC procedure described in Section 2.1 but without adding the biradicals), which gave rise to two distinct samples for each PS polymer (hence a total of four distinct samples for each impregnation batch). The thickness of the polymer films was of ~ 200 μm . Therefore, each impregnation batch contained four samples at the same time, yielding a total mass of polymer samples of ~ 440 mg per batch (200 mg for each PS powder and ~ 20 mg for each PS film). A mass of bTbK of 35–50 mg was introduced by batch, after checking that this quantity is in excess in our experimental conditions. The high-pressure vessel was closed, heated, and then filled with CO₂ to reach the experimental conditions of pressure and temperature, fixed to 200 bars and 50°C. For this purpose, CO₂ was first liquefied through a cooling unit and then pressurized using the high-pressure pump and heated before feeding the autoclave until reaching the desired pressure. The autoclave is then isolated for a predetermined impregnation duration set to 24 h. During this time, the biradicals dissolve within scCO₂ and the resulting fluid phase (CO₂/biradicals) diffuses within the polymer samples for a predetermined impregnation duration set to 24 h. The system was then depressurized in isothermal conditions. Two depressurization rates were tested, which will hereafter be referred to as *fast* (complete depressurization was achieved within ~ 5 min) or *slow* (total depressurization time of 100 min, with a controlled rate of 2 bars min^{-1}).

3 | RESULTS AND DISCUSSION

As a proof of concept, amorphous PS samples with two distinct molecular weights (35 and 280 kg mol^{-1}) were selected to compare the efficiency of the herein proposed methodology with respect to others available in the literature. In particular, Le et al. had shown that DNP signal enhancements (ϵ) on the order of 10 could be obtained using FC with TEKPol on a range of PS samples with varying molecular weights.^[29] Le et al. also showed that even higher DNP signal enhancements could be achieved using the glass-forming (GF) sample preparation, but mostly at the expense of a globally reduced *real* sensitivity enhancement,^[29] which can be conveniently expressed by the ratio of the signal-to-noise (S/N) per unit of square time of the low-temperature DNP-enhanced ssNMR experiment with respect to the S/N per



SCHEME 2 Schematic description of the experimental setup used in this study

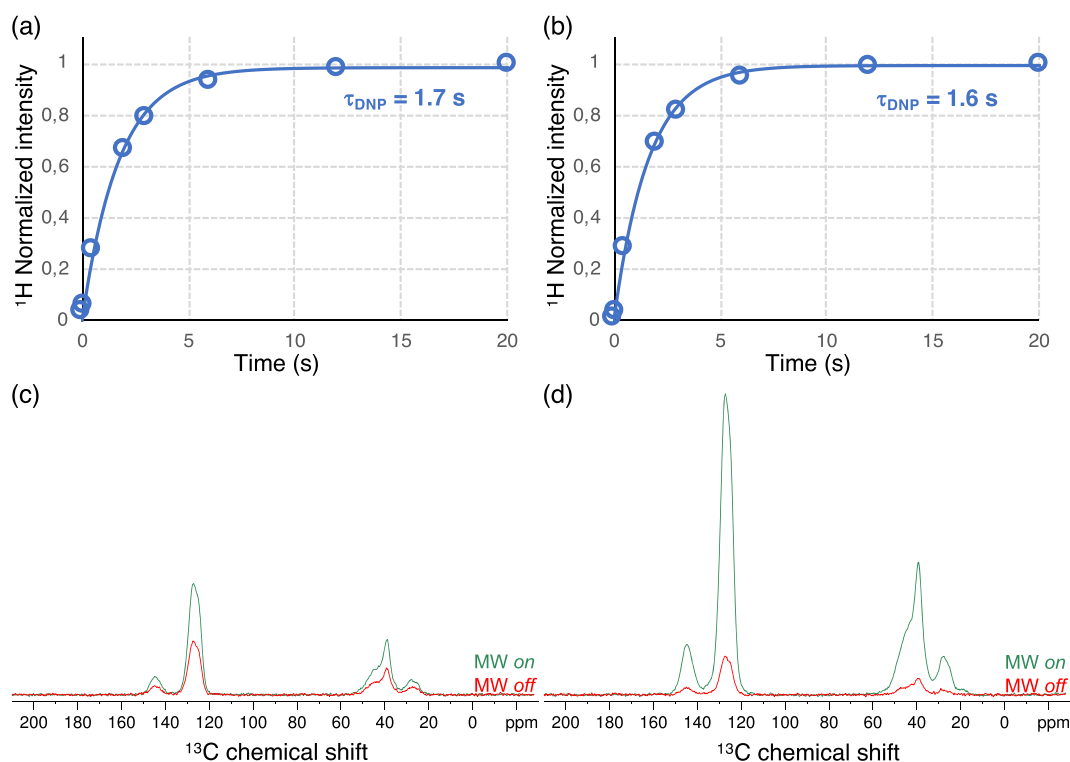


FIGURE 1 (a,b) ^1H saturation-recovery curves obtained on the PS-35k sample prepared by (a) FC and (b) i-scCO₂ (film sample with slow depressurization). (c,d) ^{13}C CP MAS spectra recorded at 10 kHz and $\sim 100 \text{ K}$ with (green) and without (red) microwave irradiation on the PS-35k sample prepared by FC (c) and i-scCO₂ (d). The same vertical scale was used in (c) and (d) for comparison.

unit of square time of the conventional ssNMR experiment recorded at room temperature without DNP.^[43] Moreover, GF has the additional drawback of requiring the use of a solvent that may give rise to observable resonances in the corresponding ^{13}C CP MAS spectrum, unless specific measures are used to remove them.^[44–47]

Figure 1 compares the results obtained by DNP ssNMR for the PS-35k sample prepared by FC and i-scCO₂ (using a film and a slow depressurization rate), respectively. First, the ^1H saturation-recovery curves obtained on both samples with the microwave field *on* (Figure 1a,b) display similar monoexponential behavior,

suggesting that bTbK is homogeneously dispersed within the polymer matrix in both cases.^[48,49] Likewise, comparison of the ^1H signal intensity in spectra obtained with rotor-synchronized ^1H MAS Hahn-echo experiments recorded with the microwave field *on*, suggest that both samples display comparable coherence lifetimes (data not shown). Second, DNP signal enhancements of 2 and 8 were measured on the $^1\text{H} \rightarrow ^{13}\text{C}$ CP MAS experiments recorded with and without microwave irradiation on the FC and i-scCO₂ samples, respectively (Figure 1c and d). In parallel, continuous-wave electron paramagnetic resonance (CW EPR) analysis indicated that the FC sample

had a lower amount of bTbK than the i-scCO₂ sample (~10 and ~20 μmol g⁻¹, respectively). The higher bTbK loading for the i-scCO₂ sample was consistent with the lower signal amplitude of its *off* ¹³C CP MAS spectrum. For these types of polymer samples,^[29] we have previously observed experimentally that DNP signal enhancements do not change drastically in this range of loadings (a maximum increase of the order of +50% is usually observed). Therefore, the reason for observing a fourfold increase in ε for samples that otherwise exhibit roughly comparable bTbK loadings is not clear to us yet.

Additional data are summarized in Figure 2 in terms of DNP signal enhancements. These data indicate that i-scCO₂ is more efficient than FC for PS-35k samples in all the experimental conditions tested herein (powder/film and fast/slow depressurization), with contents in bTbK that were on average on the order of 20 μmol g⁻¹ (±20%). Results obtained on the PS-280k samples, however, were more mixed, with ε values for the i-scCO₂ samples that were at best comparable or lower than those obtained for the FC sample, with bTbK contents below 5 μmol g⁻¹ (i.e., below the optimum of 10 μmol g⁻¹). This suggests that the experimental conditions used for scCO₂ impregnations are not optimal for such a high molecular weight sample. In fact, i-scCO₂ optimization is based on an intricate interplay between the solubility of the species to be impregnated (here, the biradicals) in the supercritical fluid (CO₂) and the partition of the solubilized impregnating species in the CO₂ and the polymer phases. Furthermore, when applied to glassy or semicrystalline polymers, scCO₂ acts as a plasticizer because the small molecule of CO₂ diffuses between the polymer chains

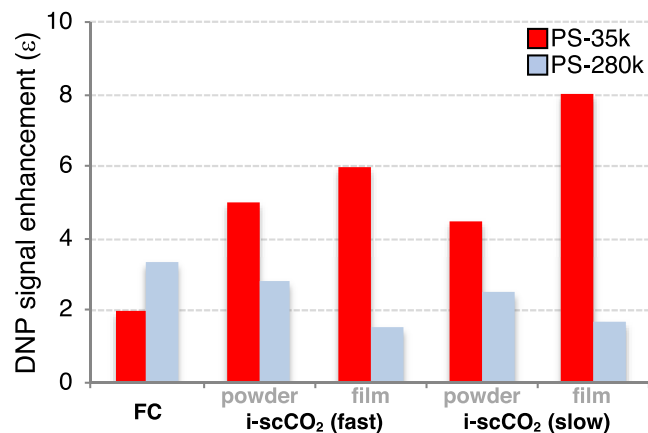


FIGURE 2 DNP signal enhancements (ε) obtained for the PS-35k and PS-280k samples prepared by FC or i-scCO₂ using bTbK. For i-scCO₂, two depressurization rates were used (fast vs. slow) on two distinct polymer morphologies (powder vs. film). Measurement uncertainty on ε determinations is ±10%.

and its sorption increases the polymer free volume. This results in a “reversible” swelling of the polymer and reduces its glass transition temperature, hereby favoring impregnation. Both the kinetics and thermodynamics of the system under study will eventually impact the impregnation efficiency, as expressed in terms of impregnation yield (i.e., the actual amount of biradicals introduced in the polymer) and quality (i.e., the homogeneity of the resulting impregnated material). The poor results obtained for PS-280k could be due to its glass transition temperature that is expected to be higher than that of its lower molecular weight counterpart.^[50] Moreover, the smaller average cavity size observed in polymers with large average molecular weights could also explain the less effective bTbK impregnation for the PS-280k samples.^[51] Interestingly, as shown elsewhere,^[52] the DNP signal enhancements obtained on all these PS samples, independently from their preparation method, could be increased by a factor of ~2 after removing part of the absorbed oxygen from the samples, reaching a ε value of 16 for the PS-35k sample prepared by i-scCO₂ (slow/film conditions). Finally, preliminary trials with TEKPol, a more efficient biradical than bTbK for DNP at 9.4 T and ~100 K, did not yield better results for these polymers, most likely due to the low solubility of TEKPol in scCO₂. This clearly calls for the design of alternative biradicals showing optimized properties not only for DNP but also for i-scCO₂.

4 | CONCLUSIONS

We have illustrated the great potential of i-scCO₂ as an efficient method for preparing polymer samples for DNP ssNMR experiments. Remarkably, the possibility of operating at relatively low temperatures (<60°C) is appealing for thermally sensitive materials such as functional/reactive or cross-linked polymers and nanostructured organic materials. Nevertheless, the methodology also has some weaknesses. First, its success depends on the balance between the solubility of the biradicals in the CO₂ supercritical phase and their affinity for the polymer materials. This could possibly translate into a low solute loading due to a partition coefficient of the solute to be impregnated in favor of the scCO₂ phase. In the case of DNP ssNMR samples, however, the targeted solute loadings remain relatively low (<1 wt%), and hence, even relatively inefficient scCO₂ impregnations could provide samples with adequate amounts of biradicals. Second, it is unlikely that the experimental conditions optimized for one type of polymer will be fully applicable to another, which may result in tedious optimization every time a new biradical/polymer system is considered. For

instance, estimation of the duration of polymer exposure to supercritical CO₂ for its complete sorption and the corresponding swelling degree should be conducted. Impregnation parameters (including pressure, temperature, impregnation duration, and depressurization rate) should also be optimized for a given biradical/polymer system. However, using as starting points the large variety of experimental conditions available in the literature for the scCO₂ impregnation of polymers, together with experimental design approaches as well as general guidelines for optimizing these conditions in the specific field of DNP ssNMR, this aspect should not prove insuperable. Clearly, further work is required at this point to improve the methodology. First, an experimental apparatus specifically tuned to our targeted application must be designed and set up to work with reduced quantities of samples, possibly in an impregnation vessel coupled with a saturator using a recirculating scCO₂ pump to enhance solute impregnation. Second, biradicals solubilities in scCO₂ should be quantitatively determined, which in turn could possibly prompt the design of alternative biradicals showing optimized properties for i-scCO₂. Finally, extension of this methodology to other types of samples, including nanoparticles or organic powders, could also be envisioned. We also note that alternative scCO₂-based techniques, derived for instance from the gas-saturated solutions (PGSS) methodology,^[53] could prove useful in this context as well. Experiments along these lines are currently in progress in our lab and will be reported in future publications.

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PEER REVIEW

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